

Chapter 1: PM_{2.5} Overview

LESSON GOAL

Demonstrate, through successful completion of the chapter review exercises, a general understanding of the composition of fine particulate matter in the atmosphere; how the components of fine particulate matter are formed; and the types of sources that contribute to the formation of fine particulate matter.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to:

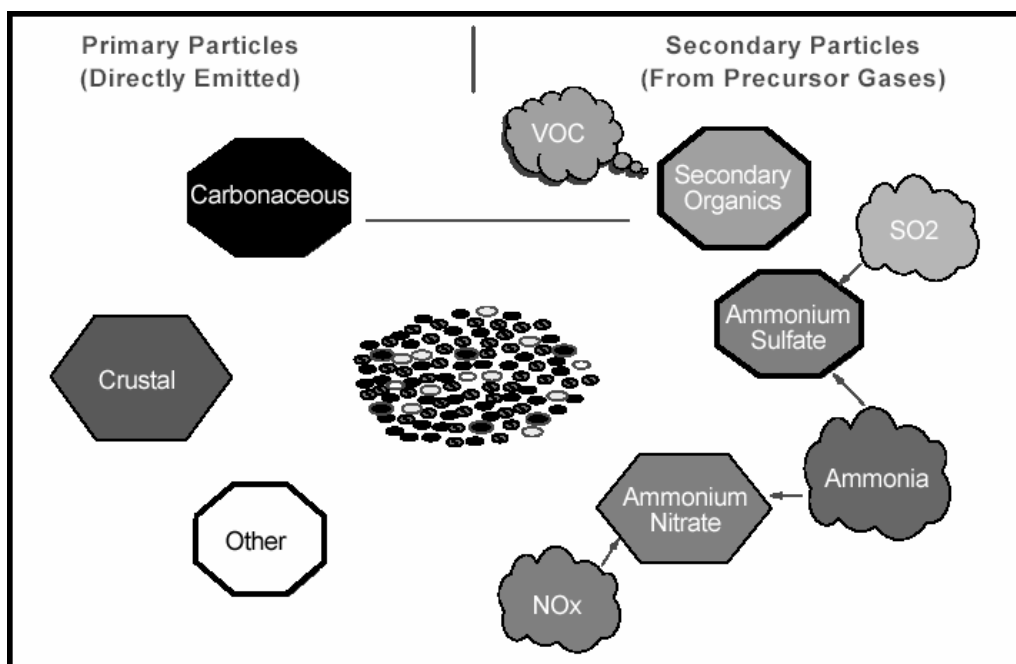
1. Explain the difference between primary and secondary particles.
2. Explain the geographical differences in PM_{2.5} concentrations.
3. Define the term “urban excess.”
4. Describe the sources that emit precursors to the formation of secondary particles.
5. Explain the difference between crustal and carbon emissions.
6. Describe possible control strategies for reducing fine particulate matter concentrations.

Chapter 1: PM_{2.5} Overview

1.1 PM COMPOSITION

In learning about particulate matter it is important to understand the difference between directly emitted or primary particles and secondary particles that are formed in the atmosphere from precursor gases. The distinction is graphically depicted in Figure 1-1. Primary particles consist mostly of elemental carbon (EC) and primary organic aerosol (POA) but will also contain crustal matter and a few other materials. Secondary particles consist of secondary organic aerosol (SOA) formed from volatile organic compounds, ammonium sulfate formed from SO₂ and ammonia gases, and ammonium nitrate, formed from NO_x and ammonia gases. The term total carbonaceous matter is used to describe the combined mass of EC, POA and SOA.

Figure 1-1. PM_{2.5} in Ambient Air



1.1.1 Urban Sites

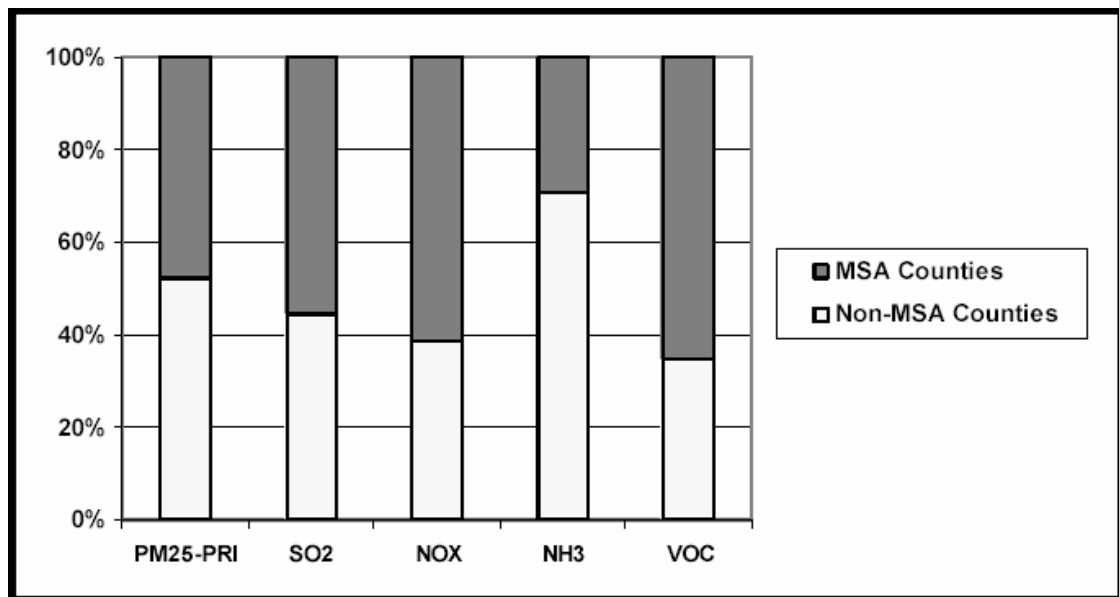
A review of data from EPA's urban speciation trends network shows that particulate matter in the eastern half of the United States is very homogenous in terms of composition. Another feature of Eastern sites is that the PM is comprised of mainly carbonaceous aerosol and ammonium sulfate in roughly comparable amounts. It is also important to note that the data shows the crustal component of PM_{2.5} is very

small in both Western and Eastern urban monitoring sites, with the exception of a few places in the southwest and the central valley of California.

1.1.2 Urban and Rural Comparisons

Figure 1-2 represents the magnitude of the emissions of primary PM and the various precursors throughout the 37 state eastern and central United States. As this figure shows, about half of the PM primary is emitted in the Metropolitan Statistical Areas (MSAs) and about half in the rural areas. This figure also shows that ammonia is the only precursor with larger emissions in the rural areas than in the urban areas. This is due to the large contribution of agriculture to ammonia emissions. However, it should be noted that there is still some ammonia in the urban areas because of agriculture in the urban areas, and mobile sources.

Figure 1-2. MSA to Non-MSA Comparison of PM Emissions



An examination of ambient monitoring data from both urban and rural sites in the speciation trends network shows that there is more sulfate than carbon in the non-urban sites. Sulfate concentrations are only slightly higher in the urban areas than in the surrounding non-urban areas; however, carbon concentrations do increase substantially in the urban areas. The conclusion from this monitoring data is that sulfate is very much a regional problem. Carbon, on the other hand, does have a regional component, there is a significant excess of carbon in the urban areas, as evidenced by the marked increase in carbon from rural to urban areas. Urban air quality data is often compared to rural air quality data by noting the amount of “urban excess” for a particular component.

This concept is illustrated using data from the Atlanta area. As shown in Figure 1-3, almost all of the sulfate is associated with the regional contribution. In other words the sulfate that you find in Atlanta is only 10-15% higher in concentration than the

sulfate that you find in the surrounding rural sites. The ammonium concentrations show the same pattern as the sulfate concentrations because most of the ammonium is associated with sulfate. The data also show that the nitrate and carbon concentrations are about twice as high in the urban areas as they are in the rural areas, a significant “excess”. The top part of the bars in Figure 1-3 shows this “urban excess.” It is also important to note that the concentration of total carbonaceous material is greater than the sulfate concentrations in Atlanta and that the concentration of crustal material is very small.

Figure 1-3. Example of “Urban Excess”

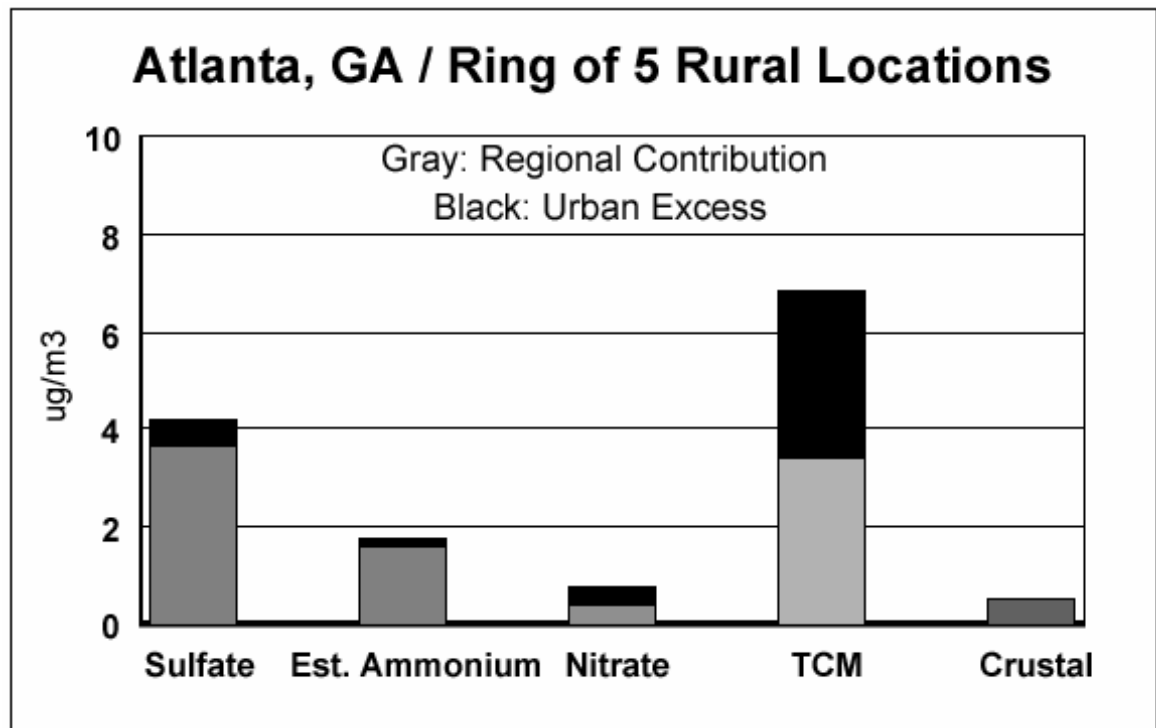
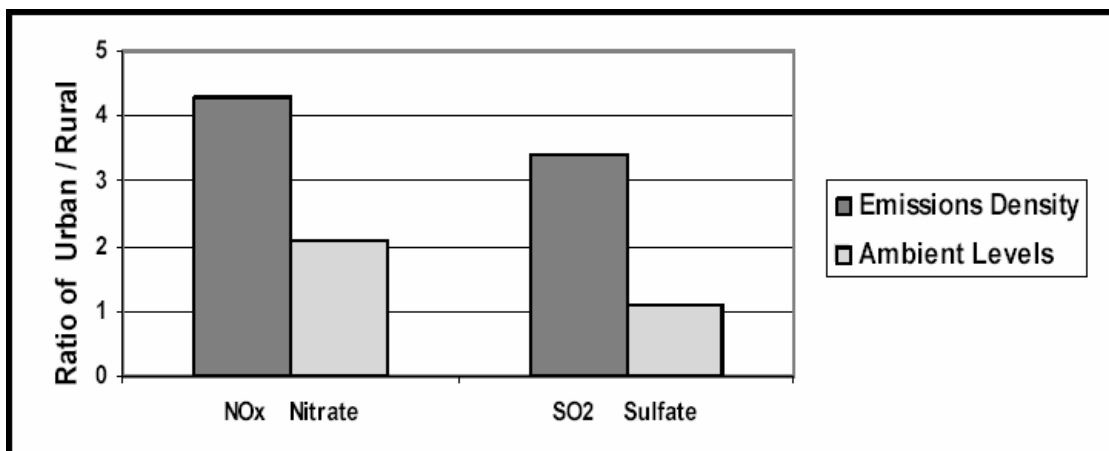


Figure 1-4 shows another comparison of urban and rural information by comparing emission densities with ambient concentrations. The density of NO_x emissions per square mile are about four times higher in urban areas than they are in the rural areas and the concentrations of nitrate are only about twice as high in the urban areas as in the rural areas. This suggests that the higher concentration of ammonium nitrate in urban areas is associated with the higher NO_x emissions in the urban areas. Sulfate has a much higher density of emissions in the urban areas, but this ratio is not reflected in the ambient data. As seen in the Atlanta example, there is virtually no urban excess of sulfate there. This lack of urban excess sulfate is found throughout the East.

Figure 1-4. Comparison of Urban –Rural Ratios



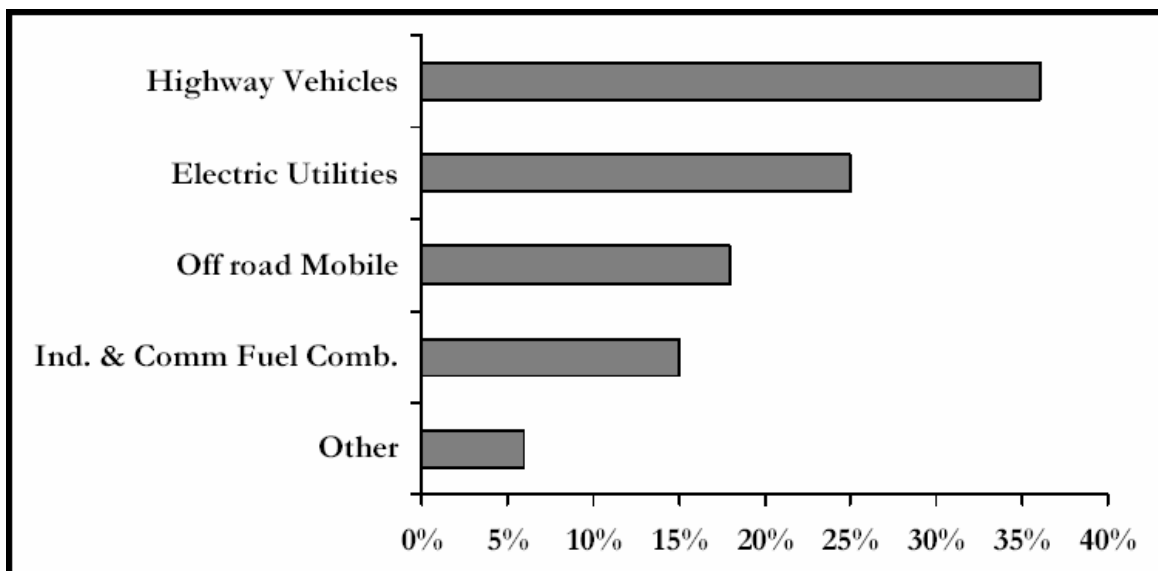
The reason for these differences between the urban excesses for nitrates and sulfates is due at least in part to the following. The NO_x to nitrate reaction occurs fairly quickly and much of the transformation occurs before it gets transported very far. Also, nitrate is a little less stable and may revert to other compounds during transport. Sulfate, on the other hand, has a very long lifetime. Once it is converted from SO₂ to sulfate it stays around, sometimes for weeks, as a sulfate particle and can be transported long distances. So, even though the emission density of SO₂ is much higher in the urban areas than it is in the rural areas, the concentrations are fairly uniform over broad geographic areas. As a result, sulfate is considered a regional pollutant in terms of the impact on PM_{2.5}.

1.2 PM_{2.5} SOURCE CATEGORIES

1.2.1 NO_x Emissions

National data indicates that NO_x emissions are about 23 million tons a year. Figure 1-5 shows that about 35% of those emissions are from highway vehicles, twenty five percent are from electric utilities, eighteen percent are from mobile sources, and fifteen percent are from industrial and commercial fuel combustion. All of these NO_x emission sources are associated with fuel combustion with the exception of the “Other” category, which is mostly emissions from industrial processes.

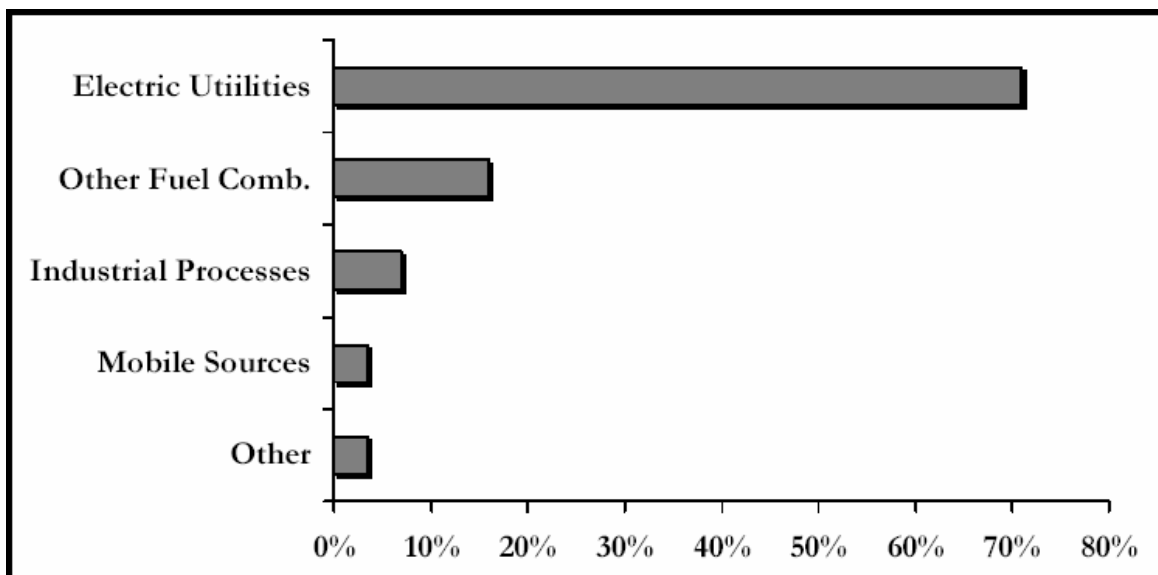
Figure 1-5. NO_x National Emissions



1.2.2 SO₂ Emissions

Figure 1-6 shows the source categories that contribute to the national SO₂ emissions. Electric utilities are responsible for about 70-75% of the emissions of SO₂. As stated previously, even though emissions from sources such as electric utilities tend to be concentrated more in the urban areas where the people live, the impacts of sulfate stretch across large geographic areas, due to the long lifetime of sulfate particles and their ability to transport long distances.

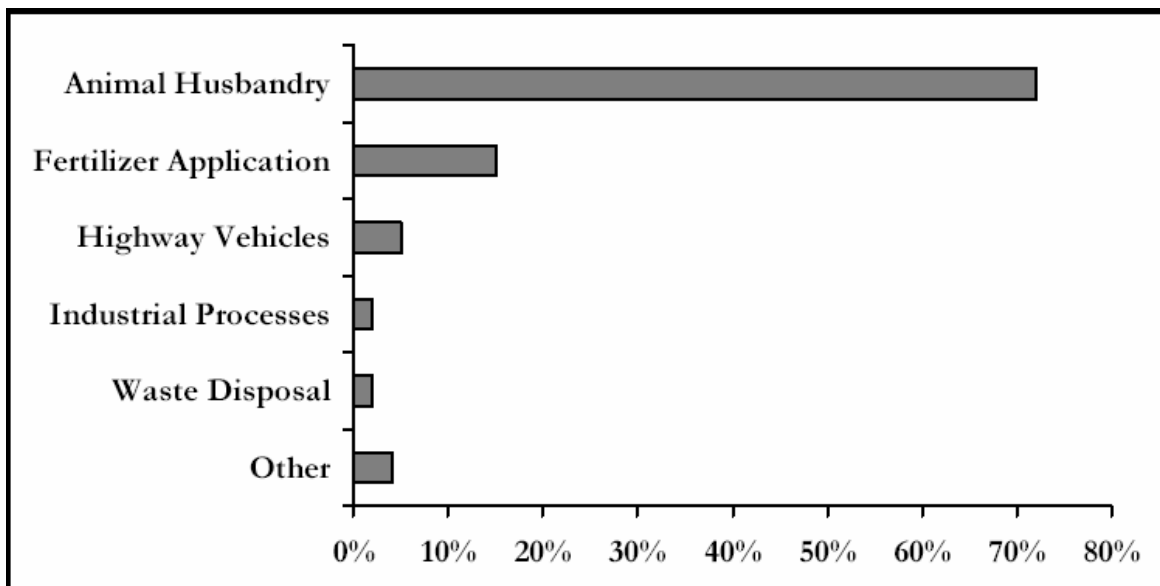
Figure 1-6. SO₂ National Emissions



1.2.3 NH₃ Emissions

Animal husbandry is by far the largest source of ammonia emissions, as indicated in Figure 1-7. The ammonia from animal husbandry operations comes from animal waste and depends on the manner in which the waste is processed. The largest single contributor to the animal husbandry category is cattle, followed by hogs and poultry. Fertilizer application is also a source of approximately 15-20% of the ammonia. There is a small percentage from highway vehicles, which can be important in an urban area.

Figure 1-7. NH₃ National Emissions



Ammonia emissions are spread out across large parts of the east and the Midwest. This is not surprising since this is the farm belt where a lot of the animals are raised. This is consistent with the pattern of measured ammonium ion deposition from the National Atmospheric Deposition Program (NADP). Specifically, there is a qualitatively good agreement between where the ammonia is deposited and where the ammonia emissions are estimated to occur.

1.2.4 Carbon and Crustal Emissions

1.2.4.1 Crustal Emissions

Crustal material mainly comes from fugitive dust. The main sources of fugitive dust are unpaved roads, agricultural tilling, construction, and wind-blown dust which is found to occur mostly in the arid areas of the west. A less significant source of crustal material is fly ash. Fly ash that comes out of a coal- or oil-fired boiler is chemically similar to crustal material.

There is a huge disparity between the crustal data in an emissions inventory and the crustal material found in ambient air quality samples. The ambient data say that there is less than a microgram per cubic meter of crustal material across most of the U.S., with

the exception of the southwest. On the other hand, the emissions data indicates that PM_{2.5} emissions are about 2.5 million tons a year, which is comparable to the carbon emissions.

This apparent anomaly can be explained by looking at what happens to the fugitive dust after it is emitted. Fugitive dust emissions are not always transported very far because they are emitted very close to the ground and get trapped in shrubbery, vegetation, buildings, etc. In short, fugitive dust emissions may not all be transported very far from where they are released. When fugitive emissions data are used in air quality dispersion models to simulate the impact of that dust several miles away, these models fail to take into account the fact that a lot of the fugitive dust is going to be deposited within a few hundred yards to a few miles of the source. It is estimated that, on average, about half of the fugitive dust emitted in eastern metropolitan areas are removed by surface features near the source. This inventory adjustment only applies when the inventory is being used in regional chemical transport modeling. Thus, as will be discussed later, this adjustment is made in the emissions processor, not in the emissions inventory.

In summary, crustal materials are a relatively small part of PM_{2.5} in the ambient air. Fugitive dust is released near the ground, and surface features often capture the dust near its source.

1.2.4.2 Carbon Emissions

Carbon is a huge component of PM_{2.5} in the ambient air. You will recall from the previous section that carbon particles are those that are primary (or directly emitted) and secondary organic aerosol (SOA) particles, which are formed in the atmosphere primarily from VOCs. Primary carbon particles are comprised of elemental (or black) carbon (EC or BC), and those that have an organic structure, primary organic aerosol (POA). On average, approximately 20% of the primary carbon emissions are EC and the other 80% are POA.

Figure 1-8 shows that primary carbon nationwide comes from wildfires, mobile sources, industrial and commercial combustion, residential heating and open burning, burning of construction debris, industrial and commercial processes; agricultural burning; and fugitive dust. Nationally, there are about 2.5 million tons per year of crustal materials emitted as compared to about 2 million tons per year of primary carbon emissions. However, the carbon emissions are found in a lot more abundance in the ambient air.

Figure 1-8. Primary Carbon in PM_{2.5}

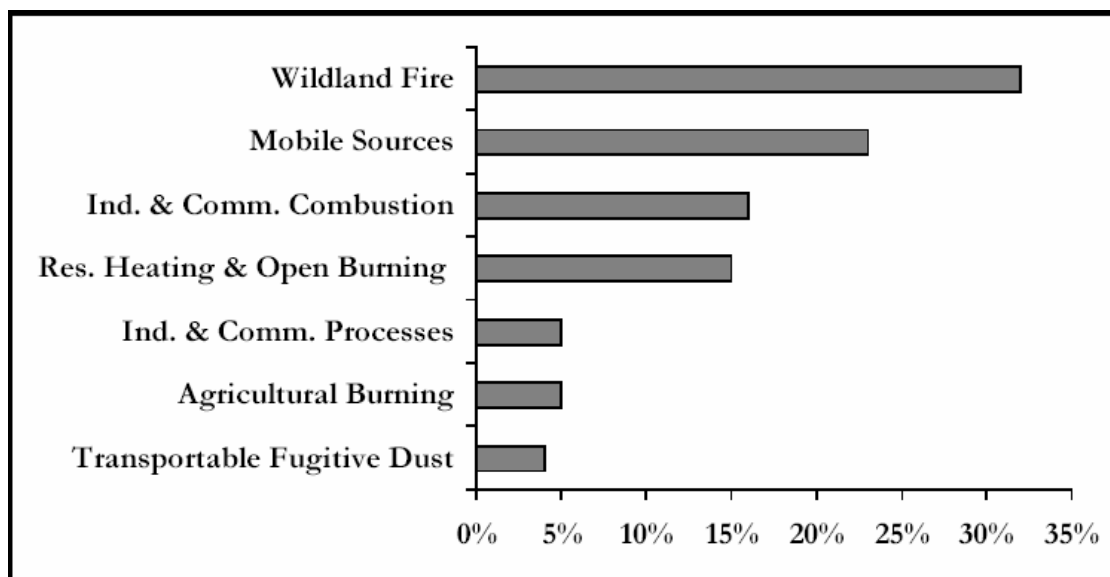


Figure 1-9 shows that the ratio of POA mass to EC mass for most sources is roughly 10 to 1. However, a major exception to this is diesel engines and diesel-powered vehicles, ships, trains and planes, where elemental carbon is a larger fraction than organic carbon. This higher elemental to organic ratio in diesels is due in part to the relatively higher combustion temperatures in diesel-fueled engines, which tends to more completely combust the organic carbon. Conversely, the lower temperature combustion processes will emit more organic matter, as a result of less complete combustion.

It is important to be aware that the organic carbon reported from analysis of a source or ambient sample does not include the oxygens, hydrogens and other elements that comprise the organic carbonaceous matter (OCM). The organic carbon matter is often called primary organic aerosol (POA). The OC to POA multiplier for “fresh” POA in the emissions is usually estimated as

$$\text{POA} = \text{OC} \times 1.2$$

to approximate the amount of oxygen and hydrogen that is found in POA emissions. In the atmosphere, these particles “age” through oxidation. As such, a different “multiplier” is often applied to the POA by (within) the chemical transport models to account for the “aging” or further oxidation of the POA emissions:

$$\text{POA} = \text{OC} \times 1.4 \text{ to } 2.4$$

Atmospheric transport and transformation models contain this additional multiplier, but only apply it to the POA, not the EC or SOA. It is important to note that the multiplier is **not** related to the model’s estimate of secondary organic aerosol formed in the atmosphere from precursor gases. It is purely to account for further oxidation of primary particle emissions as the aerosol “ages”. Transport models contain a separate module to simulate the amount of secondary organic carbon formed in the atmosphere from precursor gases and the OCM of those particles is estimated directly by that module.

The derivation of a multiplier for ambient OC is much more complicated because the sample usually contains both POA *and* SOA, but the relative proportions of each are not known. Thus, a single multiplier is applied to ambient OC, to adjust both primary *and* secondary OC that may be in the sample. The use of a single multiplier introduces error since it is likely that the multipliers would not be the same for both fractions. A multiplier of 1.4 to 2.4 is often used for ambient data.

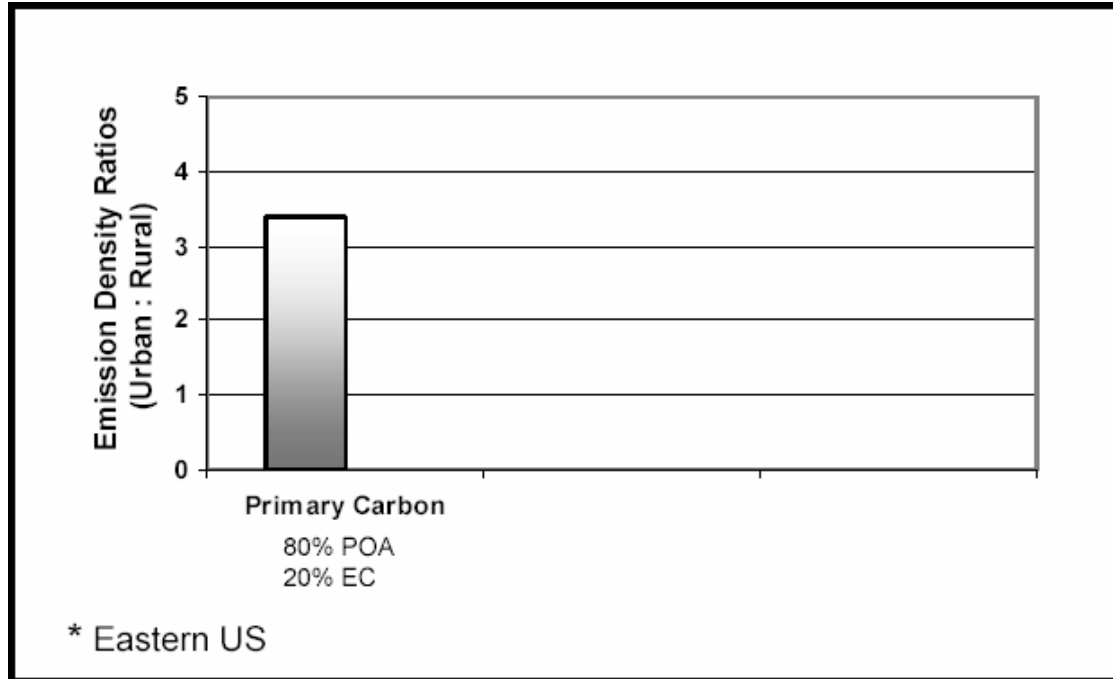
As of this writing, there is no agreed upon standard adjustment that is consistently applied in either monitoring and modeling studies.

Figure 1-9. Characteristics of Primary Carbon

Category	Ratio of Organic Carbon Mass to Elemental Carbon Mass (Average)	Potential Range of Ratios
Forest Fires	9.9	6 – 28
Managed Burning	12	6 – 28
Agricultural Burning	12	2.5 – 12
Open Burning – Debris	9.9	
Non-road Diesel Engines & Vehicles	0.4	0.4 – 3
On-road Diesel Vehicles	0.4	0.4 – 3
Trains, Ships, Planes	0.4	0.4 – 25
Non-road Gas Engines & Vehicles	14	0.25 – 14
On-road Gas Vehicles	4.2	0.25 – 14
Fugitive Dust – Roads	22	3 - 65
Woodstoves	7.4	3 - 50
Fireplaces	7.4	3 - 50
Residential Heating – Other	26	
Commercial Cooking	111	13 - 111

Figure 1-10 shows a comparison of the emission density ratios for urban carbon emissions and rural carbon emissions. There is about three times as much primary carbon emitted in urban areas as there is in the rural areas; about 80% of this is primary organic aerosol and about 20% is elemental carbon.

Figure 1-10. Primary Carbon Emission Density Ratios*



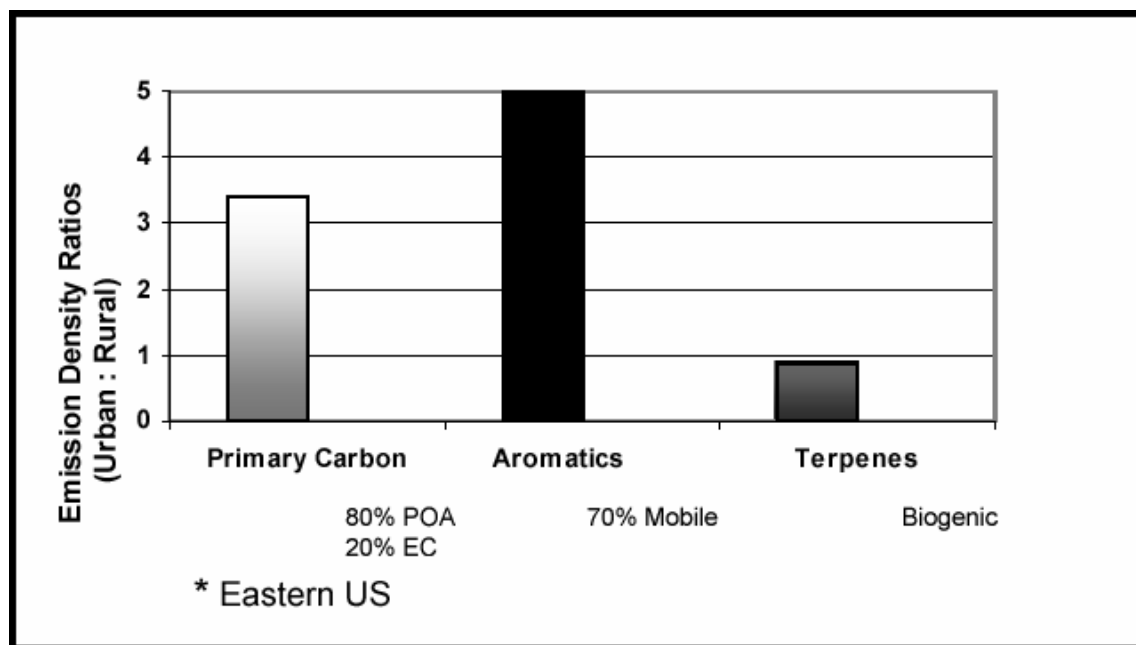
The primary particles are comprised of approximately 80 percent primary organic aerosols and 20 percent elemental carbon. Some of EPA's emission factors identify a condensable part. This represents the organics that are in the vapor phase when they are measured at stack temperatures and condense to form particles when the plume cools. Condensibles are included in the POA emissions estimate.

1.2.5 Volatile Organic Compound Emissions

Aromatics and terpenes are the VOC precursors that react to produce secondary organic aerosols. About 70 percent of aromatics come from mobile sources and include benzene, toluene, and xylene. Toluene and xylene are the two aromatics that are generally associated with secondary aerosol formation. Since the majority of these VOC precursors are emitted from cars, it is not surprising that the emission density of aromatics is about five times higher in urban areas than in the rural areas. The formation of SOA from these aromatic precursors is another potential cause of the urban excess that was discussed in Section 1.1.

Terpenes are another big source of secondary organic aerosols. Almost all terpenes are biogenic in origin in that they are emitted by a variety of vegetation. However, their emissions are not limited to rural areas. In fact, there is almost as much terpene emissions in a square mile of urban area as there is in a square mile of rural area (See Figure 1-11). This is due to the fact, despite land clearing, there are many trees in urban areas.

Figure 1-11. Comparison of Emission Density Ratios*



1.3 SUMMARY

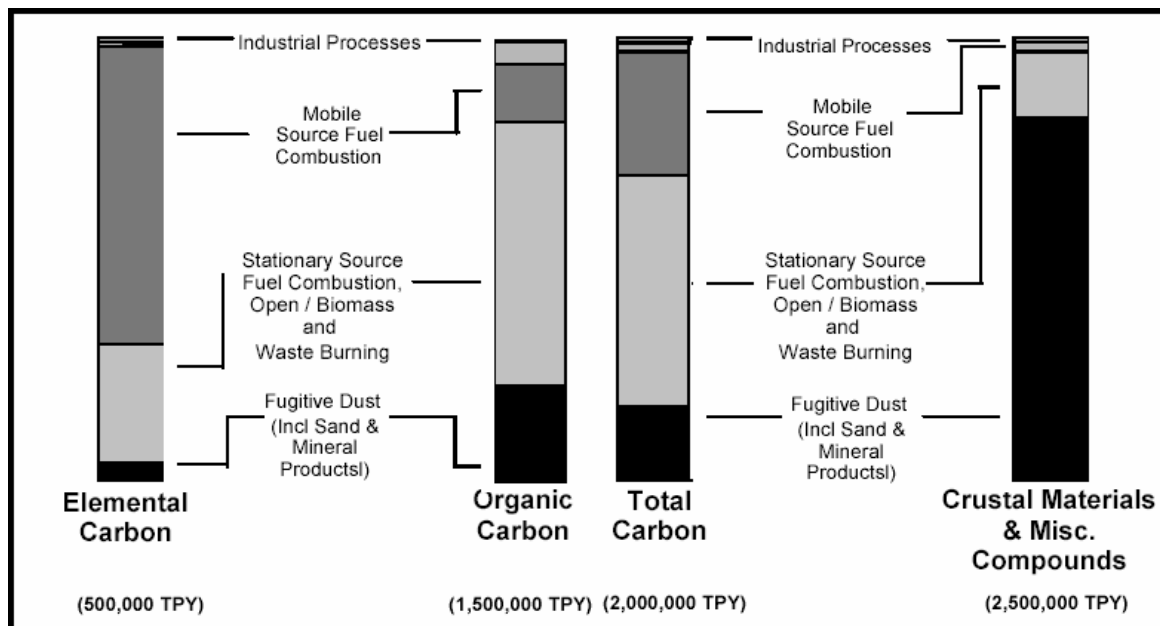
Figure 1-12 presents a summary of the larger source categories of $PM_{2.5}$ direct and precursor emissions. These are presented in no particular order; however, the larger categories are in boldfaced type.

Figure 1-12. Summary of Important PM _{2.5} Source Categories		
Direct Emissions	Precursor Emissions	
Combustion ^{a,b}	SO₂ ^c	NH₃
<ul style="list-style-type: none"> • Open Burning (all types) • Non-Road & On-Road Mobile • Residential Wood Burning • Wildfires • Power Gen • Boilers (Oil, Gas, Coal) • Boilers (Wood) 	<ul style="list-style-type: none"> • Power Gen (Coal) • Boilers (Coal) • Boilers (Oil) • Industrial Processes 	<ul style="list-style-type: none"> • On-Road Mobile • Animal Husbandry • Fertilizer Application • Wastewater Treatment • Boilers
Crustal / Metals ^b	NO_x	VOC ^d
<ul style="list-style-type: none"> • Fugitive Dust • Mineral Prod Ind • Ferrous Metals 	<ul style="list-style-type: none"> • On-Road Mobile (Gas, Diesel) • Power Gen (Coal) • Non-Road Mobile (Diesel) • Boilers (Gas, Coal) • Residential (Gas, Oil) • Industrial Processes 	<ul style="list-style-type: none"> • Biogenics • Solvent Use • On-Road (Gas) • Storage and Transport • Residential Wood • Petrochemical Industry • Waste Disposal
<p>a Includes primary organic particles, elemental carbon and condensable organic particles; also some flyash</p> <p>b Impact of carbonaceous emissions on ambient PM 5 to 10 times more than crustal emissions impact</p> <p>c Includes SO and SO and HSO condensable inorganics</p> <p>d Contributes to formation of secondary organic aerosols</p>		<p>NOTE: Categories in BOLD are most important nationally. Their relative importance varies among and between urban and rural areas.</p>

Figure 1-13 illustrates several important features of PM_{2.5} emissions. First, it shows that the majority of both elemental and organic carbon comes from combustion sources. It also shows that almost all of the crustal materials are associated with fugitive dust and very little of the total carbon is associated with fugitive dust.

Emissions of primary carbonaceous PM_{2.5} are about two million tons per year, and about a fourth of that is elemental carbon. However, the emissions of crustal materials is about 2.5M tons per year, roughly similar in magnitude. However, due the further adjustments made to the EI for carbon and crustal materials previously discussed, (carbon emissions increase and the crustal emissions are reduced), carbon is usually found in much greater quantity on ambient PM_{2.5} samples than are crustal materials.

Figure 1-13. Summary of PM_{2.5} Primary Emission Sources



The formation of secondary organics from terpenes associated with VOC emissions from vegetation occurs relatively fast. The formation of secondary organics from aromatics associated with VOC emissions from mobile sources occurs slower than the terpene reaction. From a control strategy standpoint it is important to recognize that reducing aromatics would reduce secondary organic aerosol.

Ammonium sulfate is formed from SO₂ that is emitted from the combustion of sulfur containing fuels. Compared to ozone, the sulfate forms and deposits more slowly and therefore may be transported much longer distances than either ozone or nitrate. If there were insufficient ammonia the formation product would be partially neutralized particles of ammonium bisulfate, or possibly even sulfuric acid. From a control strategy standpoint, reducing emissions of SO₂ will lower ammonium sulfate concentrations.

Ammonium nitrate is formed from NO_x that is emitted from fuel combustion. Nitrates are formed relatively quickly. If there is insufficient ammonia, the ammonia will react to form ammonium sulfate before it forms ammonium nitrate. Higher temperatures and a lower relative humidity will shift equilibrium so that less nitrate and more nitric acid will be formed. Reducing NO_x emissions may reduce nitrates, sulfates and secondary organic aerosols, but the outcomes are complicated, involve ozone chemistry and can't be generalized.

In general a reduction in VOC emissions would reduce ozone levels and that would result in less secondary organic aerosols, sulfate and nitrate formation. However, this is very complicated issue and must collectively consider ozone formation, ozone precursors, sulfates, nitrates, and the secondary organics because the reactions are interrelated.

Review Exercises

1. Which of the following is **not** a component of secondary particles that are formed in the atmosphere?
 - a. ammonium sulfate
 - b. ammonium nitrate
 - c. crustal particles
 - d. secondary organics
2. Which of the following characteristics are common to particulate matter in the eastern half of the United States?
 - a. Its composition is chemically similar across a number of urban areas
 - b. It is comprised of mostly carbon
 - c. The ammonium and sulfate components are comparable to the carbon component
 - d. All of the above
3. The density of NO_x emissions per square mile are about _____ times higher in urban areas than they are in the rural areas, but the concentrations of nitrate are only about _____ times higher in the urban areas as in the rural areas.
 - a. four, two
 - b. two, four
 - c. ten, five
 - d. three, two
4. Twenty-five percent of total NO_x emissions are associated with _____, the second largest contributor.
 - a. Highway vehicles
 - b. Farm animals
 - c. Fugitive dust
 - d. Electric utilities
5. Which of the following is the least significant source of crustal material?
 - a. Unpaved roads
 - b. Agricultural tilling
 - c. Construction
 - d. Coal and oil-fired boilers
6. Approximately _____ percent of primary carbon is elemental.
 - a. 10
 - b. 25
 - c. 50
 - d. 75

7. Which of the following sources of primary carbon has a low ratio of organic carbon mass to elemental carbon mass?
- a. Wildfires
 - b. Fugitive dust
 - c. Diesel engines
 - d. All of the above
8. Which of the following is **not** an aromatic VOC precursor to secondary organic formation?
- a. Benzene
 - b. Toluene
 - c. Terpenes
 - d. Xylene
9. Secondary organic aerosol formation _____ when the ambient temperature increases.
- a. increases
 - b. decreases
 - c. remains constant
 - d. ceases
10. _____ is (are) the only precursor with much larger emission density in rural areas than in urban areas.
- a. Terpenes
 - b. Benzene
 - c. Ammonia
 - d. Sulfates

Review Answers

1. c. carbonaceous particles
2. d. All of the above
3. a. four, two
4. d. Electric utilities
5. d. Coal and oil-fired boilers
6. b. 25
7. c. Diesel engines
8. c. Terpenes
9. a. increases
10. c. ammonia

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